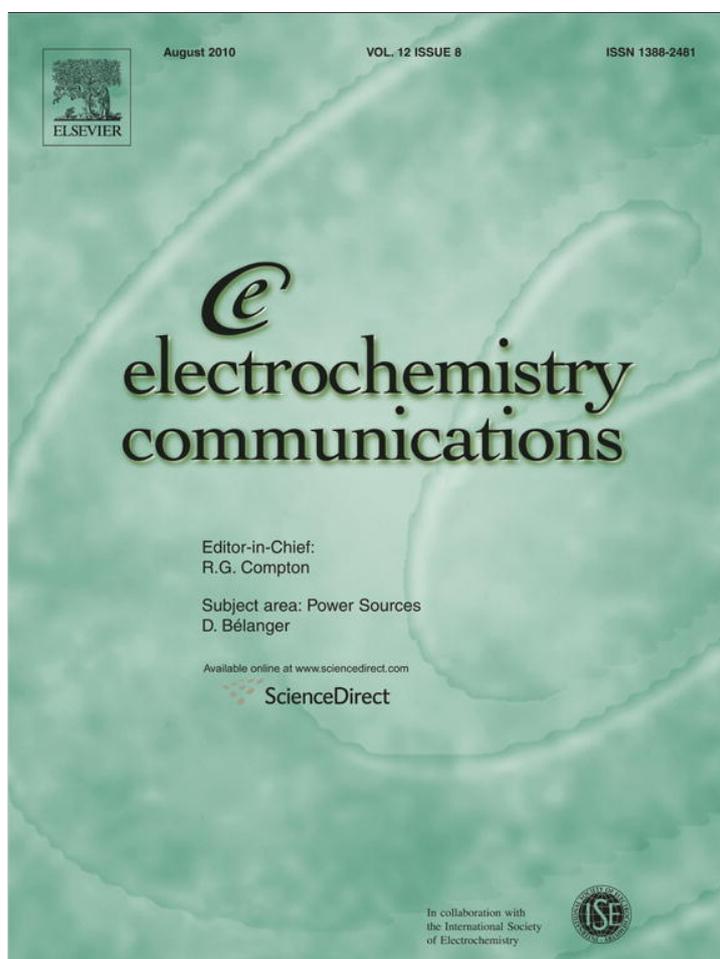


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Layer-by-layer assembly of porphyrin/layered double hydroxide ultrathin film and its electrocatalytic behavior for H₂O₂

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ABSTRACT

The ordered ultrathin film based on iron(III) porphyrin and Co–Al layered double hydroxide (Co–Al LDH) nanosheets has been fabricated *via* the layer-by-layer (LBL) method. The film modified electrode demonstrates a couple of well-defined reversible redox peaks attributed to Co(III)/Co(II), with iron(III) porphyrin serving as an efficient mediator for facilitating the electron transfer. Furthermore, it exhibits excellent electrocatalytic behavior for H₂O₂ with a wide linear range of response, high sensitivity and low detection limit.

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1. Introduction

Layered double hydroxides (LDHs) are a class of naturally occurring and synthetic materials, which can be described by the general formula $[M^{II}_{1-x}M^{III}_x(OH)_2]^{z+}(A^{n-})_{z/n} \cdot yH_2O$ (M^{II} and M^{III} are divalent and trivalent metals respectively; A^{n-} is the interlayer anion compensating for the positive charge of the metal hydroxide layers). The specific layered structure, large surface area and anion exchange properties of LDH materials make them attractive candidates as catalysts, catalyst precursors, anion exchangers, bioactive nanocomposites, electro- and photofunctional materials [1–7]. Recently, LDH materials have been used as amperometric or potentiometric sensors *via* modification on the surface of electrodes [8–10] owing to the following advantages: nontoxicity, high stability and compatibility with many functional molecules [11].

However, the application of LDHs as electroactive materials for amperometric sensors is largely restricted due to the limitation of charge transfer between LDHs and electrode. The incorporation of electroactive materials (as electron-transfer mediator) with LDHs would be one effective method to resolve this problem. Recently, the delamination of LDHs into single nanosheet has been reported [12]. This inspires us to challenge the goal of fabricating electrochemical sensors *via* alternate LBL assembly of positively charged LDH nanosheets and negatively charged electroactive species, since LBL method has been used to fabricate ordered thin films for electrochemical sensors [13,14]. In this work, the ordered ultrathin films

(UTFs) based on iron(III) porphyrin and Co–Al LDH nanosheets have been fabricated *via* the LBL method, and demonstrate its electrocatalytic properties towards reduction of H₂O₂. Herein, the positively charged Co–Al LDH nanosheets as building blocks were assembled alternately with negatively charged 5,10,15,20-tetrakis(4-sulfonatophenyl) porphyrinato iron(III) (Fe(III)-TPPS) on a pretreated ITO substrate, and the direct electrochemistry behavior of Co–Al LDH nanosheets was obtained. In addition, the Co–Al LDH/Fe(III)-TPPS film modified electrode exhibits excellent electrocatalytic performances for H₂O₂ with high sensitivity and activity. Therefore, the novel strategy in this work provides a method for fabricating UTFs with superior electrochemical properties *via* assembly of conductive complexes with nano-scale inorganic matrix, which can be potentially used in the field of sensors.

2. Experimental

2.1. Reagents and materials

4,4',4'',4'''-(porphine-5,10,15,20-tetrayl)tetrakis (benzenesulfonic acid) tetrasodium salt hydrate (TPPS) was purchased from Sigma–Aldrich Company. Analytical grade chemicals including CoCl₂·6H₂O, Al(NO₃)₃·9H₂O and NaOH were purchased from the Beijing Chemical Co. Limited and used without further purification.

2.2. Preparation of the Co–Al LDH/Fe(III)-TPPS film modified electrode

The Co–Al LDH nanosheets were prepared by the method reported previously [15]. Fe(III)-TPPS was synthesized by the insertion of iron

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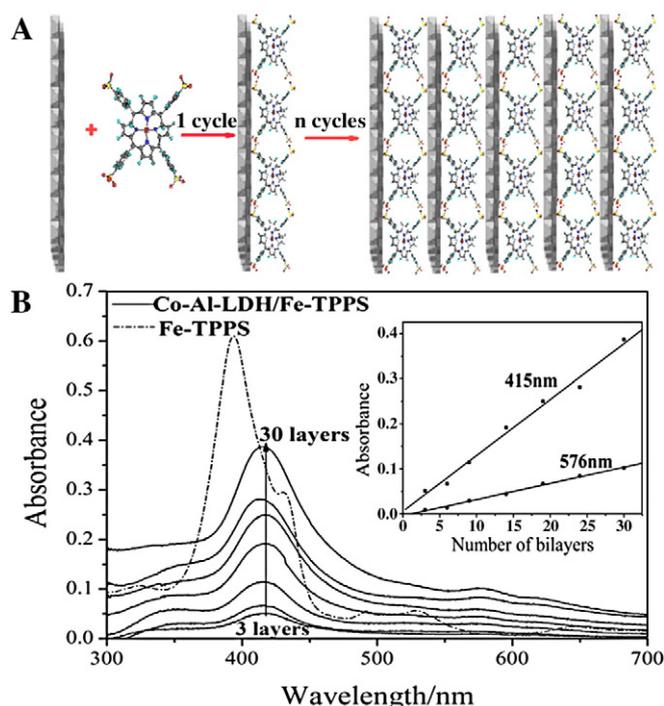


Fig. 1. (A) Schematic representation for the LBL assembly of $(\text{LDH}/\text{Fe}(\text{III})\text{-TPPS})_n$ UTFs; and (B) UV-vis absorption spectra of the $(\text{LDH}/\text{Fe}(\text{III})\text{-TPPS})_n$ UTFs along with different bilayer number (n) on quartz glass substrates. The inset shows plots of the absorbance at 415 and 576 nm vs. n respectively.

into the free-base TPPS ligand using ferrous chloride tetrahydrate in dimethylformamide (DMF), as described by Adler and Longo [16]. The $(\text{LDH}/\text{Fe}(\text{III})\text{-TPPS})_n$ UTFs were fabricated by applying the LBL assembly technique. The substrate was immersed into the colloidal

suspension of LDH nanosheets (1 mg/mL) for 10 min followed by washing with water, and then dipped into a Fe(III)-TPPS aqueous solution (0.01 mg/mL) for 10 min and washed thoroughly. Subsequently, a series of deposition operations for LDH nanosheets and Fe(III)-TPPS were repeated n times to obtain $(\text{LDH}/\text{Fe}(\text{III})\text{-TPPS})_n$ UTFs (Fig. 1A). The resulting films were dried in nitrogen gas flow.

2.3. Characterization techniques

X-ray diffraction (XRD) patterns were recorded by a Rigaku XRD-6000 diffractometer, using Cu $K\alpha$ radiation ($\lambda = 0.15418$ nm) at 40 kV, 30 mA. The UV-vis spectra were collected in a Shimadzu U-3000 spectrophotometer. The morphology of thin films was investigated using a scanning electron microscope (SEM Hitachi S-4700) with the accelerating voltage of 20 kV. The surface roughness was studied using the atomic force microscopy (AFM) software (Digital Instruments, Version 6.12). The electrochemical measurements were performed using a CHI 660C electrochemical workstation (Shanghai Chenhua Instrument Co., China). A conventional three-electrode system was used, including a modified ITO glass as the working electrode, a platinum foil as the auxiliary electrode and a saturated Ag/AgCl electrode as the reference electrode. All electrochemical measurements were carried out in a NaOH solution (Milli-Q water: > 18 M Ω cm) at room temperature (ca. 20 $^\circ\text{C}$).

3. Results and discussion

3.1. Structural and morphological characterization of the $(\text{LDH}/\text{Fe}(\text{III})\text{-TPPS})_n$ UTFs

The growth of the multilayer films was monitored by UV-vis absorption spectra (Fig. 1B). The $(\text{LDH}/\text{Fe}(\text{III})\text{-TPPS})_n$ films exhibit a strong absorption band at ~ 415 nm, corresponding to the characteristic Soret band of Fe(III)-TPPS. Compared with the $\pi\text{-}\pi^*$ absorption band at 393 nm of pristine Fe(III)-TPPS in aqueous solution, the

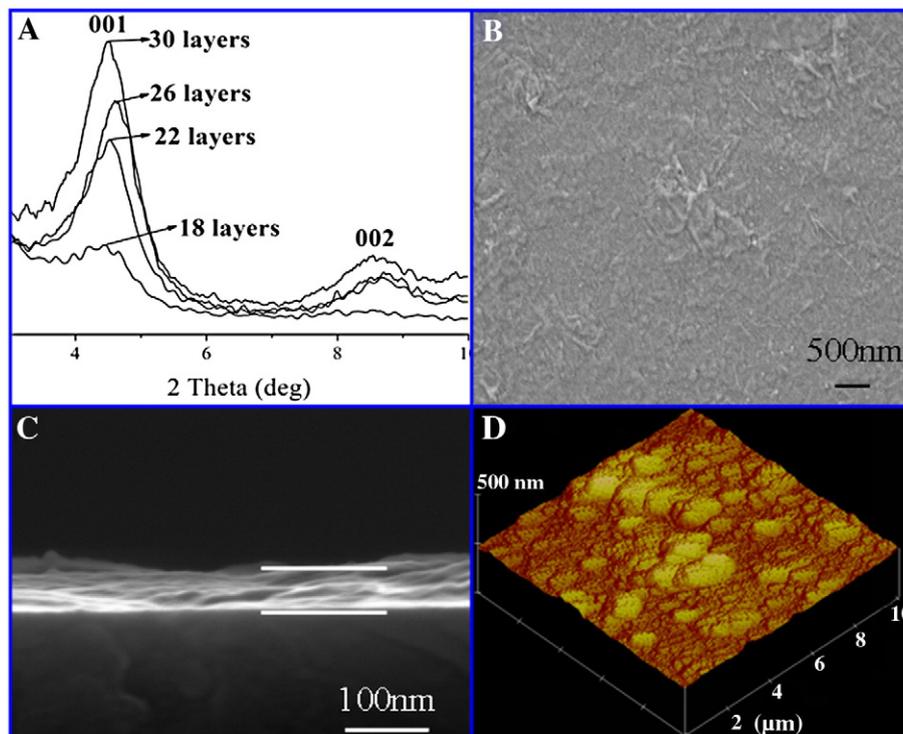


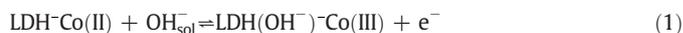
Fig. 2. (A) XRD patterns for the $(\text{LDH}/\text{Fe}(\text{III})\text{-TPPS})_n$ UTFs deposited on quartz glass substrates; (B) top view and (C) side view of SEM image for the $(\text{LDH}/\text{Fe}(\text{III})\text{-TPPS})_{30}$ UTF; and (D) AFM image of the $(\text{LDH}/\text{Fe}(\text{III})\text{-TPPS})_{30}$ UTF.

obvious red-shift for the multilayer film can be attributed to the strong interaction between individual molecules in the densely packed films. The intensities of the absorption bands at 415 and 576 nm (the Q band) correlate linearly with the bilayer number (Fig. 1B, inset), indicative of a stepwise and regular deposition procedure with almost equal amount of Fe(III)-TPPS incorporated in each cycle. XRD patterns (Fig. 2A) of the multilayer films illustrate the evolution of a Bragg peak at $2\theta = 4.4^\circ$ ($d_{001} = 1.95$ nm), which is attributed to a so-called superlattice reflection of the uniform and periodic layered structure of the UTFs [12,17]. The reflection intensity increased progressively with the increase of bilayer number, further confirming the successful fabrication of the (LDH/Fe(III)-TPPS) $_n$ UTFs.

The film thickness and surface morphology of the (LDH/Fe(III)-TPPS) $_n$ UTFs were further investigated by scanning electron microscopy (SEM) and atomic force microscopy (AFM). A top view of SEM image for the (LDH/Fe(III)-TPPS) $_{30}$ film (Fig. 2B) shows that the film surface is continuous and uniform, with the thickness of ~ 58 nm obtained from a side view image (Fig. 2C). The average repeating distance was therefore calculated to be ~ 1.93 nm for one bilayer, which is consistent with the periodicity result obtained from XRD measurement (1.95 nm). The AFM topographical image ($10 \mu\text{m} \times 10 \mu\text{m}$) of the (LDH/Fe(III)-TPPS) $_{30}$ UTF is shown in Fig. 2D, from which the value of root-mean-square (rms) roughness was found to be ~ 27.5 nm, indicating a relatively smooth surface of the film.

3.2. Electrocatalytic performances for H_2O_2

Fig. 3A shows the cyclic voltammograms (CVs) of different electrodes in 0.1 M NaOH at 0.1 V s^{-1} . No obvious electrochemical response was observed for either bared ITO (curve a) or Fe(III)-TPPS/ITO (curve b). The Co–Al LDH/ITO shows one pair of redox peaks which are not well-resolved, corresponding to the reduction and oxidation of cobalt (curve c):



However, the (Co–Al LDH/Fe(III)-TPPS) $_{10}$ /ITO gives a couple of well-defined reversible redox peaks at 0.51 V and 0.47 V (curve d, Fig. 3A). A rather low ΔE_p (40 mV) was obtained, and the ratio between the anodic and cathodic peak current is 1.01. This indicates that Fe(III)-TPPS serves as a kind of conductive complex facilitating charge transfer. In order to further verify the redox process described in Eq. (1), cyclic voltammograms were carried out in NaOH solution with various concentrations (Fig. 3B). Negative shifts in both anodic and cathodic peak potentials were observed upon increasing the concentration of OH^- , indicating that OH^- plays a key role in the redox process of cobalt.

The growth of (LDH/Fe(III)-TPPS) $_n$ film on the surface of ITO electrode was also monitored by CVs. Both the reduction and

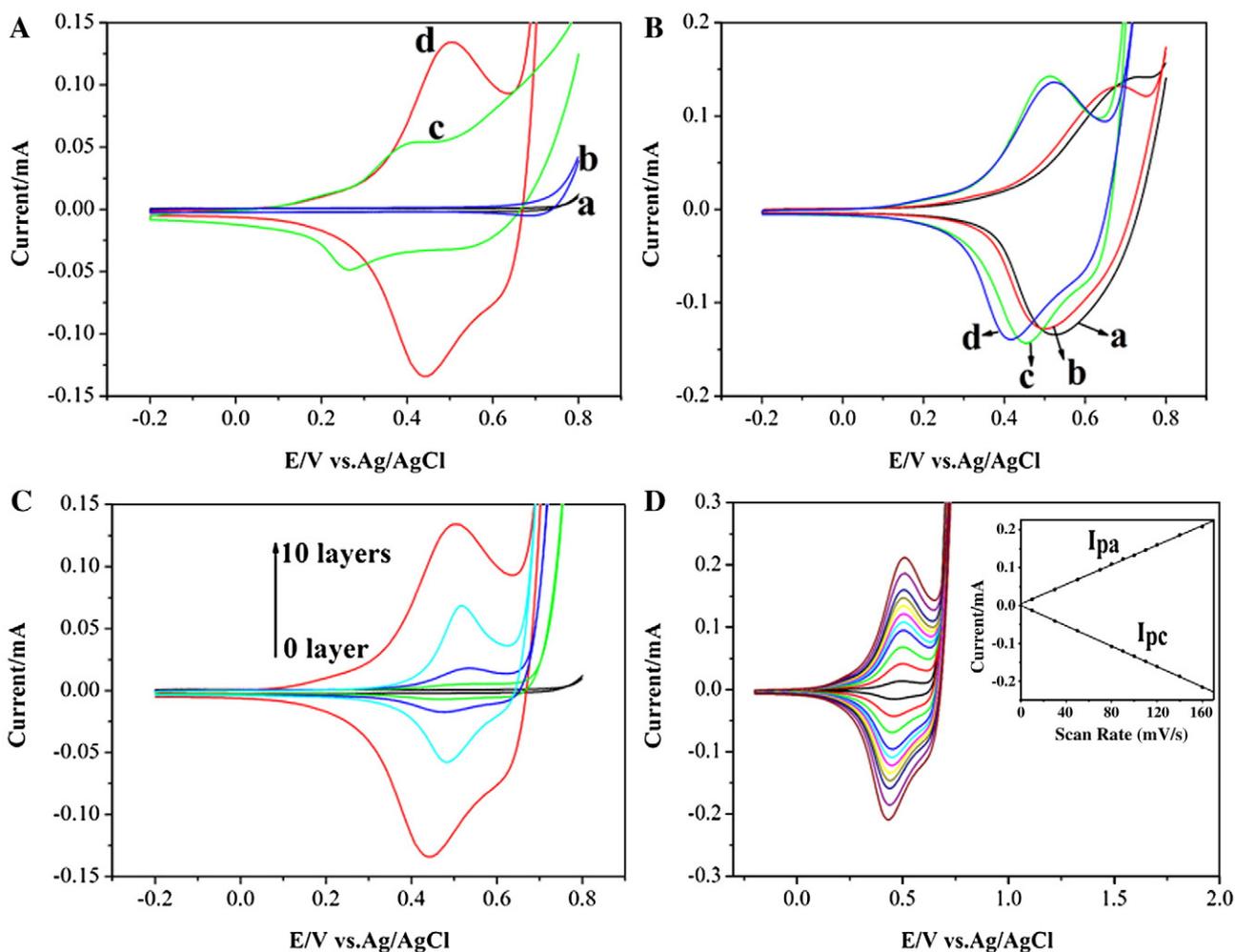


Fig. 3. (A) CVs of (a) bare ITO, (b) Fe-TPPS/ITO, (c) Co–Al LDH nanosheet/ITO and (d) (Co–Al LDH/Fe(III)-TPPS) $_{10}$ /ITO in 0.1 M NaOH at a scan rate of 0.1 V s^{-1} ; (B) CVs of (Co–Al LDH/Fe(III)-TPPS) $_{10}$ /ITO in (a) 0.001 M, (b) 0.01 M, (c) 0.1 M and (d) 1.0 M NaOH at a scan rate of 0.1 V s^{-1} ; (C) CVs of (Co–Al LDH/Fe(III)-TPPS) $_n$ /ITO with different bilayer number (n): 0, 2, 4, 6 and 10 in 0.1 M NaOH at a scan rate of 0.1 V s^{-1} ; and (D) CVs of (Co–Al LDH/Fe(III)-TPPS) $_{10}$ /ITO with scan rate ranging from 0.01 to 0.12 V s^{-1} ; inset: plots of peak current vs. scan rate in 0.1 M NaOH.

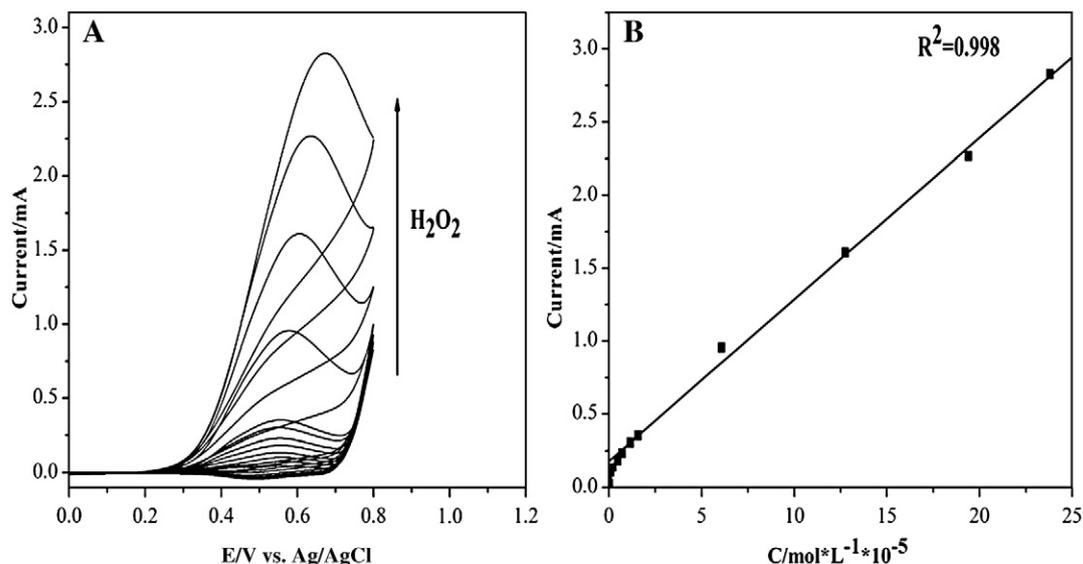


Fig. 4. (A) CVs of the (Co–Al LDH/Fe(III)-TPPS)₁₀/ITO in 0.1 M NaOH solution with different concentrations of H₂O₂; scan rate: 0.1 V s⁻¹. (B) The linear relationship between the anodic peak current and concentration of H₂O₂.

oxidation peaks increase linearly upon increasing bilayer number (n) up to 10 cycles (Fig. 3C), suggesting the uniform and ordered growth of the UTFs. All the low ΔE_p values (~ 40 mV at 0.1 V s⁻¹) suggest a fast electron transfer in the multilayer films. This property may be attributed to the formation of the uniform films by effective LBL assembly of LDH nanosheets with Fe(III)-TPPS, in which Fe(III)-TPPS serves as mediator facilitating the electron transfer. The effect of scan rate on the electrochemical response of the (LDH/Fe(III)-TPPS)₁₀ film is shown in Fig. 3D. It was found that a linear relationship between the anodic (or cathodic) peak current and the potential sweep rate was obtained, indicating a surface-controlled process.

The electrocatalytic oxidation of H₂O₂ at the (Co–Al LDH/Fe(III)-TPPS) _{n} /ITO was studied by cyclic voltammetry. Fig. 4A depicts the CVs for the (Co–Al LDH/Fe(III)-TPPS)₁₀ film with the presence of various H₂O₂ concentrations in a 0.1 M NaOH solution. The anodic peak current increased linearly with the increase of H₂O₂ concentration in the range from 4.9×10^{-7} to 2.4×10^{-4} M, with the linear regression equation of i_{pa} (mA) = $13.5 + 1.0c$ (10^{-6} M), $r = 0.998$ (Fig. 4B). The detection limit (DL) is 1.8×10^{-8} M obtained from calibration curves for H₂O₂ ($S/N = 3$). Moreover, the (Co–Al LDH/Fe(III)-TPPS)₁₀ modified electrode exhibits high thermal stability (95% of its initial electrocatalytic current remains after heating at 100 °C for 1 h) and long-term stability (97% of its initial current remains after 20 days).

4. Conclusions

In summary, well-ordered Co–Al LDH/Fe(III)-TPPS UTFs have been fabricated by the electrostatic LBL self-assembled technique. The structural and surface morphology studies show that the ultrathin film is continuous and uniform with long range stacking order in the normal direction of the substrate. The Co–Al LDH/Fe(III)-TPPS film modified electrode demonstrates a couple of well-defined reversible redox peaks. Furthermore, the modified electrode exhibits electrocatalytic behavior for H₂O₂ with high sensitivity, thermal and long-term stability. Therefore, this work provides a novel and efficient

strategy to incorporate electron mediator into an inorganic layered matrix, for the purpose of accelerating electron transfer between electroactive species and electrode. It is anticipated that the method in this work can be used for the design and fabrication of various nano-scale electronic devices or sensors.

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